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Abstract

C_{70}, like C_{60}, can exist in a number of oxidation states including C_{70}^{1-}, C_{70}^{2-}, C_{70}^{3-} and C_{70}^{4-}. We have discovered unique visible and near-IR absorption transitions which appear upon reduction of C_{70}. These transitions are observed upon one, two, three and four-electron electrochemical reductions of C_{70}. In contrast to C_{60}, however, the electronic properties of C_{70} are less well understood. In particular, previous theoretical studies of C_{70}^{1-} failed to predict the existence of the near-IR transition we observe in the spectrum of C_{70}^{1-}. In this paper, in addition to presenting the, heretofore unreported, spectra of the various C_{70} anions, we attempt a first-order explanation of the energies and intensities of the various spectral absorptions; this explanation is based on the published molecular orbital diagram for neutral C_{70} and a structural distortion that we suggest occurs upon reduction of C_{70}.

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Abstract

C_{70}, like C_{60}, can exist in a number of oxidation states including C_{70}^{1-}, C_{70}^{2-}, C_{70}^{3-} and C_{70}^{4-}. We have discovered unique visible and near-IR absorption transitions which appear upon reduction of C_{70}. These transitions are observed upon one, two, three and four-electron electrochemical reductions of C_{70}. In contrast to C_{60}, however, the electronic properties of C_{70} are less well understood. In particular, previous theoretical studies of C_{70}^{1-} failed to predict the existence of the near-IR transition we observe in the spectrum of C_{70}^{1-}. In this paper, in addition to presenting the, heretofore unreported, spectra of the various C_{70} anions, we attempt a first-order explanation of the energies and intensities of the various spectral absorptions; this explanation is based on the published molecular orbital diagram for neutral C_{70} and a structural distortion that we suggest occurs upon reduction of C_{70}.

We have recently reported that the anionic forms of C_{60} (i.e. C_{60}^{n-} where n = 1-4) show near-IR absorption bands that are characteristic for each oxidation state.[1] We have since carried out analogous spectroelectrochemical investigations on the C_{70} anions. C_{70}, like C_{60}, can undergo electrochemical reduction to C_{70}^{1-}, C_{70}^{2-}, C_{70}^{3-} and C_{70}^{4-}.[2] Previous investigations of C_{70}^{1-} (the only C_{70} anion to be studied spectroscopically, to date), failed to detect any unique electronic transitions related to this species within the spectral ranges studied.[3-5] We present in this paper the first observations of unique visible and near-IR transitions for the C_{70} anions, including a previously-undetected near-IR transition for C_{70}^{1-}. In addition to presenting the spectra of the various C_{70} anions, we attempt a first-order rationalization of the energies and intensities of the spectral absorptions; this explanation is based on modifications of the calculated molecular orbital (MO) diagram for neutral C_{70}.[6]

C_{70} (99.9%) was obtained from Texas Fullerenes. C_{70} solutions (ca. 0.15 mM) were prepared in benzonitrile that was 0.1M in Bu_4NPF_6 supporting electrolyte. Spectra of the various C_{70} species were obtained at room temperature using the method described previously.[1] Briefly, an optically-transparent thin-layer electrochemical cell[7] was mounted within the sample chamber of a Hitachi 3501 UV-visible-near-IR spectrometer. A spectrum of C_{70} was first obtained with the cell at open circuit. Cyclic voltammetric experiments were then run to determine the electrode potentials necessary to quantitatively reduce C_{70} to the mono, di, tri and tetravalent anion. These voltammograms were essentially identical to those presented in the literature for C_{70}.[2] Potentials of -1.0, -1.6, -2.2 and -2.9 V (vs. Ag/Ag$^+$)[1] were used to generate the C_{70}^{1-}, C_{70}^{2-}, C_{70}^{3-} and C_{70}^{4-} species, respectively. Each of the C_{70} anions, generated in this manner, was stable during the lifetime of the

spectroelectrochemical experiment in rigorously-deoxygenated solutions, and could be subsequently reoxidized and re-reduced through appropriate potential control.

As previously reported,[8] the UV-visible spectrum of C_{70} shows strong absorptions at 330, 358, 378 and 468 nm (Figure 1, curve A). The near-IR region for C_{70} is featureless. In contrast, all of the C_{70} anions show absorption bands in the near-IR and/or visible regions (Figures 1 and 2). This is, apparently, the first time these bands have been described in the literature. Indeed, the only spectral data for the C_{70}^{n-} species currently in the literature is for C_{70}^{1-}.[3-5] These prior reports do not, however, describe the strong absorption we observe at 1368 nm (Figure 1, curve B), because data were obtained at wavelengths below 1300 nm. The wavelengths and extinction coefficients of the absorptions of the C_{70} anions are presented in Table I. The magnitude of these extinction coefficients (>2,000 $M^{-1}cm^{-1}$) indicate that the electronic transitions leading to these absorptions are symmetry allowed.

A portion of the Hückel calculated MO diagram of the D_{5h} C_{70} molecule is shown in Figure 3A.[6] The HOMO is the completely-filled a_2'' orbital and the LUMO is the a_1'' orbital. The HOMO —> LUMO transition is forbidden and the first allowed transition, a_2'' —> e_1'', must be of sufficiently weak oscillator strength that it is not readily observed. Transitions from high-lying occupied orbitals to higher unoccupied orbitals account for the UV-visible absorptions in the spectrum of C_{70} (Figure 1, curve A). These transitions have not been assigned previously and are not the subject of this report.

A number of theoretical methods have been used to predict the absorption spectrum of C_{70}^{1-}.[3-5] Unfortunately, these theoretical analyses failed to predict the experimentally-observed spectrum. For example, Greaney and Gorun[4] used Self Consistent Field-Hartree-Fock (SCF-HF)

calculations[9] on neutral C_{70} to predict the spectrum of the monoanion; this analysis suggests that there should be no near-IR transitions for C_{70}^{1-}.[4,5] Furthermore, this analysis predicts a HOMO --> LUMO transition at 2200 cm^{-1}. Both of these predictions are not consistent with the observed spectral data, as we have observed an allowed transition in the near-IR spectrum of C_{70}^{1-} (Figure 1, curve B) and the 2200 cm^{-1} IR transition was not detected[4,5] for C_{70}^{1-}. Kato, et al.,[3] used CNDO/S calculations on neutral C_{70} to predict a single HOMO —> LUMO transition at 2840 nm for C_{70}^{1-}. However, we have collected spectral data out to 3200 nm and do not observe any spectral absorptions beyond 1500 nm for C_{70}^{1-}.

The failure of these prior theoretical analyses to accurately predict the absorption spectrum of C_{70}^{1-}, leads us to conclude that the MO diagram of C_{70}, obtained from SCF-HF[9] and CNDO/S[3] calculations, is not directly applicable to the monoanion. Furthermore, the MO diagram for C_{70} obtained from Hückel calculations[6] is also not directly applicable to C_{70}^{1-} (Figure 3A). Addition of one electron to the Hückel MO diagram for C_{70} should populate the a_1'' orbital. From a_1'', however, there are no allowed transitions in the near-IR ($a_1'' \longrightarrow e_1'$, a_1' are forbidden). Thus, it is impossible to rationalize the experimentally-observed near-IR absorption spectrum of C_{70}^{1-} by simply adding an electron to any of the existing MO diagrams of C_{70}.[3-6,9] Because of the inadequacies of these previous theoretical analyses in treating C_{70}^{1-}, we have taken an approach that is analogous to that used in our successful interpretation of the spectra of the C_{60}^{n-} anions.[1] In this approach, it is assumed that addition of an electron to C_{70} causes a geometrical distortion of the molecule that reduces symmetry.

The experimental absorption spectrum for C_{70}^{1-} can be rationalized if it is assumed that addition of an electron to C_{70} causes a lowering of the

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symmetry from D_{5h} to C_{5v}.[10,11] Distortion from D_{5h} to C_{5v} symmetry occurs through the loss of the mirror plane perpendicular to the principal five-fold axis. With this type of distortion, the $C_{70}{}^{1-}$ molecule can exist as a dipolar anion (not supported in D_{5h}). It is conceivable that the driving force for this distortion arises from ion pairing between $C_{70}{}^{1-}$ and its associated countercation or interactions with solvent dipoles. That is, the electrostatic interaction with the countercation may polarize the $C_{70}{}^{1-}$ anion, creating the dipolar anion described by C_{5v} symmetry. If this is true, we would expect that the solvent and electrolyte would play a major role in the appearance of the various spectral transitions for the C_{70} anions.

We are currently examining solvent and supporting electrolyte effects on the near-IR transitions of both C_{60} and C_{70}. At this time, however, we note that the near-IR transition observed for $C_{70}{}^{1-}$ appears at the same wavelength in benzonitrile and dichloromethane solutions. Furthermore, the transition energy remains constant in the presence of tetrabutyl ammonium, tetraethyl ammonium, and lithium cationic supporting electrolytes. While these studies are not exhaustive, they suggest that the distortion that occurs upon reduction of C_{70} may be an inherent feature of the fullerene anions.

In the C_{5v} configuration, the electron added to C_{70}, to make $C_{70}{}^{1-}$, occupies an a_2 orbital (Figure 3B). The electron in the a_2 orbital is allowed a single transition that should appear in the near-IR region.[6] We have assigned the experimentally-observed near-IR absorption at 1368 nm to this C_{5v}-allowed $a_2 \longrightarrow e_1$ electronic transition (Figure 1, curve B). Further support for the C_{5v} configuration of $C_{70}{}^{1-}$ arises from the fact that we do not observe any absorptions in the far-visible region of the $C_{70}{}^{1-}$ spectrum; transitions from $a_2 \longrightarrow a_1$, e_2 (predicted to occur at ca. 700 nm)[6] are forbidden in C_{5v}. Distortion from D_{5h} symmetry is also supported by the red-shift

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and broadening of the UV-visible transitions in the spectrum of C_{70}^{1-} (Fig. 1).
A similar red-shift and broadening was observed in the 330 nm transition of
C_{60} upon reduction and was attributed to reduced symmetry in C_{60}^{1-}.[1]

The C_{5v} MO diagram can also be used to rationalize the spectra of the
other C_{70} anions.[11, 12] The spectrum of C_{70}^{2-} is shown in Figure 2, curve A.
The peak at 1368 nm, observed for C_{70}^{1-}, quantitatively disappears, and new
peaks appear in the visible at 670 nm[13,14] and the near-IR at 1170 nm.
Based upon ESR measurements, C_{70}^{2-} is S=1.[15] Consequently, the electrons
must be unpaired and two configurations can be postulated. In one scenario,
the two unpaired electrons are found in an asymmetric ground state
configuration, $a_2^1 e_1^1$. However, the predicted near-IR transitions for this
configuration are not consistent with the observed C_{70}^{2-} spectrum. The
second scenario assumes a symmetric ground state[1] in which the electrons
are found in the e_1 orbital as shown in Figure 3C. In this e_1^2 arrangement,
the allowed near-IR and visible transitions, $e_1 \longrightarrow e_1$, a_1 and $e_1 \longrightarrow a_1$, e_2,
should be observed. The energy of the e_1 orbital must be lowered enough,
relative to the a_2 orbital, to overcome electron pairing energy. Therefore, the
near-IR transitions of the divalent species ($e_1 \longrightarrow e_1$, a_1) should be found at
higher energy than in C_{70}^{1-}. This accounts for the shift in the near-IR
transition from 1368 nm for C_{70}^{1-} to 1170 nm for C_{70}^{2-}. The energies of the
LUMO+1 (e_1) and LUMO+2 (a_1) orbitals, as shown in Figure 3C, are
predicted to lie very close in energy.[6] Therefore, although two allowed near-
IR transitions are expected, they appear as a single unresolved peak (Figure
3C). Similarly, the visible transitions, assigned as $e_1 \longrightarrow a_1$, e_2, appear as a
broad, ill-defined absorption centered at 670 nm.

The spectra of the electrochemically generated C_{70}^{3-} and C_{70}^{4-} species
are shown in Figure 2, curves B and C, respectively. The peak positions of

the visible and near-IR absorptions remain at the same energy as in the spectrum of C_{70}^{2-} (a shoulder does appear at 760 nm in the spectrum of C_{70}^{3-} that quantitatively disappears upon reduction to C_{70}^{4-}). This suggests that the added electrons occupy the half-filled e_1 orbital. From this model, we would predict that C_{70}^{3-} would be S=1/2 $(e_1)^3$ and C_{70}^{4-} would be S=0 $(e_1)^4$. ESR measurements of these anions could be used to test these configurations. The visible transitions at 670 nm increase in intensity as C_{70}^{2-} is reduced to the trivalent and tetravalent forms. In contrast, the near-IR transitions at 1170 nm decrease in intensity and broaden as electrons are added to the e_1 orbital. These changes in absorption intensity may be caused by changes in oscillator strength result-ing from population of π^* orbitals.

It is particularly difficult to rationalize the remarkable similarity between the spectra of the di, tri and tetravalent anions. In our first-order approximation presented above, we have attributed this similarity to a progressive filling of the C_{5v} e_1 orbital. Intuitively, however, we would expect the addition of the third and fourth electrons to shift the energies of the various electronic transitions with respect to the spectrum of C_{70}^{2-}.[16] Nevertheless, the electronic transitions appear at the same energy in the spectra of the C_{70}^{2-}, C_{70}^{3-} and C_{70}^{4-} species. We do note a change in the visible absorption of C_{70}^{3-} (a reproducible shoulder appears at 760 nm that is not apparent in the C_{70}^{2-} and C_{70}^{4-} spectra; Figure 2B). If this feature resulted from further reduction in the symmetry of C_{70}^{3-}, shifts in the 670 and 1370 nm absorptions should be seen;[11] these shifts were not observed. At this time, we are unable to explain the feature at 760 nm in the spectrum of C_{70}^{3-}.

In conclusion, it is important to note that the Hückel calculations, upon which the first-order analysis presented here are based, are imperfect

with regard to predicting exact orbital energies. Therefore, although our analysis, using a modified Hückel MO diagram, qualitatively explains the experimentally-observed spectra, other more rigorous methods may lead to a better quantitative description of the electronic transitions of the C_{70} anions. Obviously, the best theoretical treatment of the MO diagram of the C_{70} anions would be obtained from calculations on the anions themselves. These calculations, however, are complicated by the number of atoms (seventy), and the somewhat ambiguous role of solvent and ion-pairing.

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10. Wilson, E.B.; Decius, J.; Cross, P. *Molecular Vibrations*, Dover Press: New York, 1955; p 337.

11. Other subgroups of D_{5h}, including D_5 ($D_{5h} \supset D_5$) and C_{2v} ($D_{5h} \supset C_{2v}$), were considered, but these were not consistent with the observed spectra.

12. We note that the transitions observed for the di, tri and tetravalent anions are also consistent with the ground state D_{5h} C_{70} MO diagram. In this configuration, the unpaired electrons would occupy the e_1'' orbital, lowered in energy below the a_1'' orbital. Allowed transitions to the a_2'' (visible) and e_1' (near-IR) orbitals can also explain the observed spectra of the multivalent anions. We have **not** ruled out this configuration, but for the sake of consistency, we show the proposed MO diagram of C_{70}^{2-} (Fig. 3C) as C_{5v}.

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14. It is interesting to note the similarity between the visible absorption we observe at 670 nm for the multivalent C_{70} anions and the visible absorption seen at ca. 700 nm for photoexcited C_{70} in reference 13. Although the authors did not assign this absorption as other than an $S_1 \longrightarrow S_n$ transition, the similarity between the photoexcited C_{70} spectrum and the spectra of the multivlaent C_{70} anions suggests that the $S_1 \longrightarrow S_n$ transition may result from a transition from an electron excited into an e-type orbital.

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16. These energy shifts would be expected from (a) electron pairing stabilization, (b) populating a π^* orbital which lowers bond order (c) the degeneracy of the C_{70}^{3-} species which should Jahn-Teller distort[1] and (d) increasing solvent and ion-pairing effects on the multivalent anions. Any or all of these effects should lead to variations in the observed absorption energy.

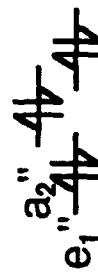Table I. Spectral data for the various C_{70} species in Benzonitrile.[a]

Species	λ max (nm)	Extinction Coefficient ($M^{-1}cm^{-1}$)
C_{70}	330	31,000
	358	23,000
	378	31,000
	468	17,000
C_{70}^{1-}	1368	4,000
C_{70}^{2-}	1170	7,200
	670	2,600
C_{70}^{3-}	1170	5,800
	670	4,600
C_{70}^{4-}	1170	3,000
	670	6,000

[a] The average uncertainty in ε measurements is ca. 20%.

Absorbance (Arbitrary Units)

Wavelength (nm)
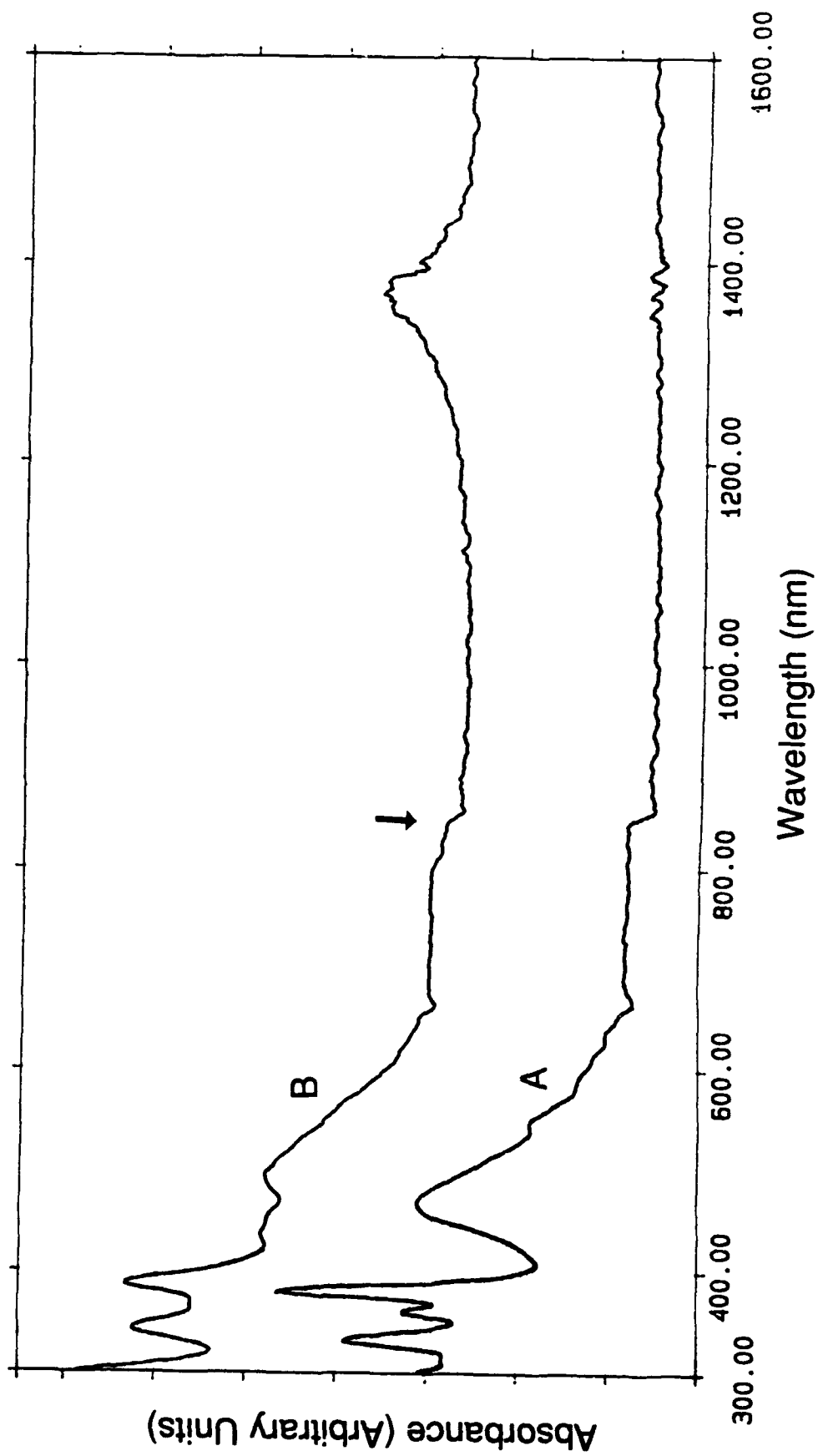
Neutral C₇₀   D_{5h}
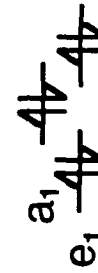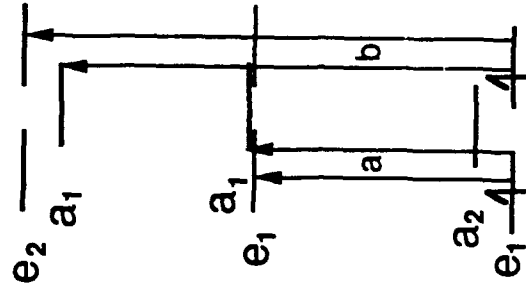
C₇₀ Monoanion   C_{5v}
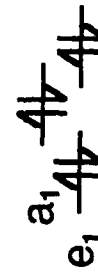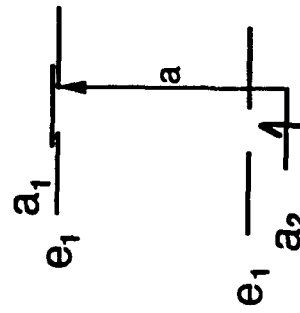
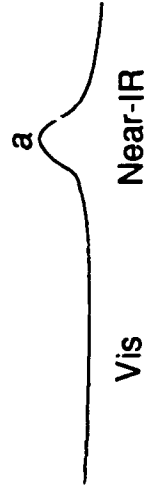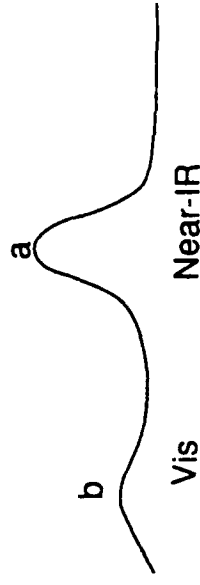C₇₀ Dianion   C_{5v}

Figure Captions

Figure 1.   UV-visible-near-IR absorption spectra for (A) C_{70} and (B) C_{70}^{1-} obtained in benzonitrile/0.1M Bu_4NPF_6. A blank sample of the supporting electrolyte solution was used for background subtraction. The feature at 840 nm, indicated by the arrow, corresponds to an instrument detector change.

Figure 2.   Visible-near-IR absorption spectra for (A) C_{70}^{2-}, (B) C_{70}^{3-} and (C) C_{70}^{4-} obtained in benzonitrile/0.1M Bu_4NPF_6. A solution of the supporting electrolyte containing neutral C_{70} was used for background subtraction. The feature at 840 nm, indicated by the arrow, corresponds to an instrument detector change. Note absorbance scale is 0.7 relative to Figure 1.

Figure 3.   (A) Relevant portion of the molecular orbital diagram of C_{70}.[6] Proposed molecular orbital diagram for (B) C_{70}^{1-} and (C) C_{70}^{2-}. The transitions in B and C are labeled and assigned to the simulated visible-near-IR spectrum placed above each diagram.